Study on sublimation of solid electrolyte (AgI)(0.5)-(AgPO3)(0.5) with Knudsen effusion mass spectrometry

RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2009; **23**: 147–150
Published online in Wiley InterScience (www.interscience.wiley.com) DOI: 10.1002/rcm.3865

RCM

Study on sublimation of solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ with Knudsen effusion mass spectrometry

Ugo Bardi, Stefano Caporali and Alexander Tolstogouzov*
Department of Chemistry, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy

Received 3 October 2008; Revised 28 October 2008; Accepted 7 November 2008

Knudsen high-temperature mass spectrometry was used to study the process of sublimation of a solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$. Monoatomic iodine ions were found to be the dominant species in the electron ionization mass spectra below 600°C. With an increase in temperature, the relative content of phosphorus oxide ions, mainly $[PO]^+$ and $[P_4O_{10}]^+$, increased. Under further heating, we observed silver iodide and iodine dimer ions together with phosphorus dimer and tetramer ions and clusters $[IPO_2]^+$, $[IP_2]^+$, $[I_3P]^+$. Using the experimental logarithmic dependencies of ion signal intensities versus the reciprocal absolute temperature of the effusion cell, the apparent sublimation enthalpies $\Delta_s H$ of the ions giving the most intense signals were estimated. Copyright © 2008 John Wiley & Sons, Ltd.

Solids that exhibit high ionic conductivity in the range of 10^{-4}–10^{-1} S cm^{-1} (where S means *Siemens*, a unit of electrical conductivity measurement) are classified as superionic solids or solid electrolytes.[1] These solids are involved in the manufacturing of fuel cells, electrolytic cells, heat-generators, gas-sensors, and other applications. Amorphous-glassy electrolytes like $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ are used in the microelectronic industry for the fabrication of resistive switching devices[2] and as high brightness ion emitters.[3]

Methods for the synthesis and the study of the physico-chemical properties of the solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ have been reported.[4,5] However, little information is available concerning the thermodynamic properties and sublimation kinetics of this electrolyte. Apart from the practical importance of such data for the deposition of thin films and sandwich structures, they are of fundamental interest for understanding how clusters form in the vapour phase.

Knudsen effusion mass spectrometry[6–8] has proved to be a powerful tool for studying the stability of gaseous molecules, the thermodynamics of condensed phases and, more generally, evaporation processes of complex materials such as solid electrolytes. Recently, this method was used in our laboratory for the investigation of imidazolium-based ionic liquids[9] and for gold assaying.[10] The goal of the present work was to study the mass composition and thermodynamics of the vapour species formed by sublimation of a solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$. We report the results obtained via Knudsen cell mass spectrometry in the temperature range from 500 to 650°C.

*Correspondence to: A. Tolstogouzov, Department of Chemistry, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.
E-mail: alexander.tolstoguzov@unifi.it

EXPERIMENTAL

Samples of the amorphous-glassy electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ were synthesized according to the procedure described in the literature.[4,5] As source materials, we used $AgNO_3$, AgI and $(NH_4)_2HPO_4$. Silver nitrate (99.9 wt. %) was obtained from Sigma-Aldrich (Milan, Italy) and the other two salts were prepared in our laboratory. In order to obtain a thoroughly mixed powder the components were carefully crushed in an agate mortar and then melted in a platinum crucible. After gas evolution, the melt was kept at 500°C for 10 h and subsequently quenched in a stainless steel mould at room temperature. The purity of the samples, estimated by scanning electron microscope/energy dispersive using X-ray (SEM/EDX), was better than 99 wt. %, and the density was found to be ca. 5 g cm^{-3}.

Details of our custom-built Knudsen effusion mass spectrometer have been published elsewhere.[10] In brief, an LFT 10 linear time-of-flight analyser with mass resolution $M/\Delta M \geq 500$ (FWHM) by Stefan Kaesdorf (Munich, Germany) equipped with an electron ionization ion source ($E_{el} = 5$–90 eV) was used to record mass spectra. For the efficient detection of heavy molecules with masses up to m/z 1000 the ions were accelerated to a maximum energy of 8 keV before hitting the detector (a two-stage microchannel plate; Burle, Lancaster, PA, USA). In the course of gold assaying[10] we have estimated the detection limit of our set-up to be within the range of $(5$–$10) \times 10^{-3}$ at. % for coinage metals like Cu, Ag, and Au.

In our experiments, samples weighing 30–50 mg were placed into a 2 cm^3 tantalum cell with an effusion orifice of 1 mm in diameter. The Clausing factor for this cell was 0.9, and the sample-to-orifice ratio was 30–35. The measurements were carried out at every 25°C at temperatures ranging from 500 to 650°C. The cell was maintained at a constant temperature for 5–10 min, and then four mass spectra, over the mass range m/z 1–500, were recorded sequentially. In

RCM

every series, the last spectrum was measured with the shutter closed (denoted as a blank or background spectrum). The results of the evaporation tests were defined as the difference between the average values of the 1st to the 3rd spectra and the background spectrum. The relative error in the estimation of average peak intensities was within ±(3–5)%.

For most experiments, a 70 eV electron beam was used for ionization of the vapour species effusing from the cell. The pressure in the analytical chamber was maintained at 5×10^{-6} Pa during the measurements.

RESULTS AND DISCUSSION

The average peak intensities of the main positive ions detected in the molecular beam are shown in Table 1. All data have been scaled to the intensities of the $[I]^+$ ions, which are given the value of 10^2 at all temperatures. The peak intensity is measured as the integral of the area under the peak over a threshold of 10 counts. A dash in the intensity column in Table 1 means that the intensity of a given ion is less than 10^3 times the intensity of the monoatomic iodine ions.

In Table 1, we can observe ions related to the thermal decomposition and the subsequent electron ionization of the constituent parts of the solid electrolyte – AgI ($[I]^+$, $[I]^{2+}$, $[I_2]^+$, $[AgI]^+$) and $AgPO_3$ ($[P_2]^+$, $[P_4]^+$, $[PO]^+$, $[PO_2]^+$, $[P_4O_9]^+$, $[P_4O_{10}]^+$). Also observed were complex associative ions composed of iodine, phosphorus and phosphorus dioxide ($[IP_2]^+$, $[IPO_2]^+$). Mono- and diatomic iodine ions were easily detectable in our experiments, in contrast to the data reported in Butman *et al*.[11] for the sublimation of cesium iodide single crystals. In that case, the $[I]^+$ ion was found only at signal intensities close to the noise level, and $[I_2]^+$ ions were not detected at all.

With an increase in the effusion cell temperature, phosphorus oxide ions began to be dominant, especially the monoxide $[PO]^+$, which surpasses in intensity the monatomic iodine ions at temperatures above 600°C. At temperatures above 700°C, we observed an ion peak at *m/z* 412 (with relative intensity 0.2), which could be interpreted as $[I_3P]^+$.

Table 1. Average signal intensities of the main positive ions measured in the saturated vapour over the solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ as a function of the effusion cell temperature (the electron ionization energy $E_{el} = 70$ eV, the intensity of $[I^+]$ ions is accepted as 10^2 at all the temperatures)

		T, °C			
Ion	*m/z*	500	550	600	650
$[I]^{2+}$	63.5	7.9	10	13.2	13.2
$[I_2]^+$	254	–	0.4	5.5	23.3
$[AgI]^+$	234 + 236	–	–	2.9	4.0
$[PO]^+$	47	4.0	18.2	118	131
$[P_2]^+$	62	–	–	–	3.0
$[PO_2]^+$	63	–	–	15.0	17.7
$[P_4]^+$	124	–	–	–	2.2
$[IP_2]^+$	189	–	–	–	2.7
$[IPO_2]$	205	–	–	15.5	13.7
$[P_4O_9]^+$	268	0.1	0.4	20.8	23.4
$[P_4O_{10}]^+$	284	0.9	3.6	32.9	20.5

Our estimate, based on the previous experiments with evaporation of coinage metals and gold alloys,[10] indicates that at temperatures over 650°C the partial pressure of most gaseous components into the effusion cell could well exceed 10 Pa. This value is an upper limit of molecular flow in the cell orifice. Under these conditions, the intense iodine-containing ions were also measured in the background spectra. Since the cell used in our experiments was not totally vapour-proof, at increased pressures the evaporated species could also reach the ionization chamber of mass spectrometer when the shutter was closed. For this reason, we did not consider here data obtained over 650°C. For the $[AgI]^+$ ions, however, we have reported data collected up to 750°C because in that case the background spectra demonstrated the absence of silver iodine ions, even at these temperatures.

Figure 1 shows the intensities *J* of iodine-containing (Fig. 1a) (we use the symbol *J* for the intensity in order to avoid confusion with the symbol *I* of iodine atoms) and phosphorus-containing (Fig. 1(b)) ions in the form of $\ln(J \cdot T)$ against the reciprocal absolute temperature *T* of the effusion cell. Using these data we estimated the apparent sublimation enthalpies $\Delta_s H$ of ions as:[12]

$$\Delta_s H = -R \cdot \Delta \ln(J \cdot T)/\Delta(1/T) \quad (1)$$

where *R* represents the gas constant. The $\Delta\ln(J \cdot T)/\Delta(1/T)$ values were calculated from the slopes of the straight lines approximating the experimental dependencies.

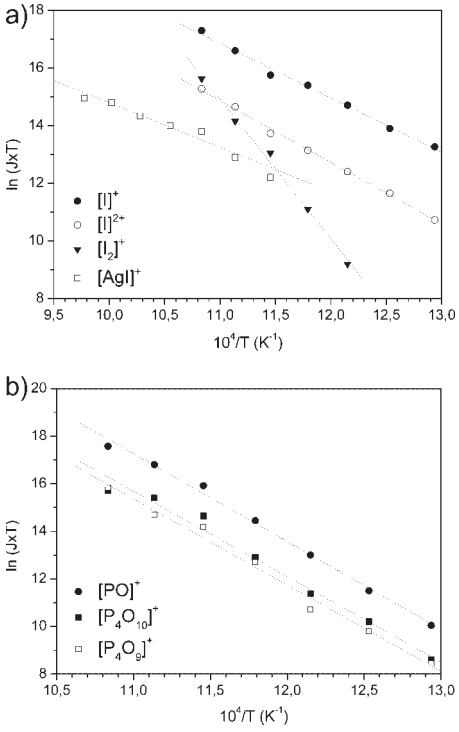

Figure 1. Temperature dependencies of the ion intensity (arbitrary units) in 70 eV electron ionization mass spectra of iodine-containing (a) and phosphorus-containing (b) species effused from the Knudsen cell containing solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$.

DOI: 10.1002/rcm

Table 2. Apparent enthalpies of sublimation estimated for most important ions (electron ionization energy $E_{el} = 70$ eV)

Ion	T, K	$\Delta_s H$ (T), kJ mol^{-1}
$[PO]^+$	773–923	307 ± 10
$[P_4O_9]^+$	773–923	298 ± 15
$[P_4O_{10}]^+$	773–923	301 ± 15
$[I]^+$	773–923	157 ± 6
$[I]^{2+}$	773–923	178 ± 4
$[I_2]^+$	823–923	403 ± 17
$[AgI]^+$	773–1023	126 ± 8

Table 2 shows the apparent sublimation enthalpies of the main ion species measured in the vapour phase over the $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ sample. As shown in Table 1, all the phosphorus oxide ions exhibit approximately the same $\Delta_s H$ values, which greatly exceed the apparent sublimation enthalpies of the iodine-containing ions with sole exception of the iodine dimers $[I_2]^+$. For such ions $\Delta_s H$ was found to be larger than 400 kJ mol^{-1}.

In Fig. 1 a small deviation of the experimental data from linearity is observed in the high-temperature range, especially for the phosphorus-containing ions. That probably indicates the transition from molecular to molecular-viscous flow through the cell orifice. In that case an internal friction begins to have an influence on the characteristics of molecular beam.[13]

On the basis of our experimental data, we can examine in greater detail the processes occurring under the heating of $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ samples and following electron ionization of the evaporated species. Thermal decomposition of silver iodide on the surface of a solid electrolyte with incongruent sublimation of iodine atoms can be considered as the dominant process at temperatures below 600°C:

$$AgI(s) \Leftrightarrow Ag(s) + I(g) \quad (2)$$

The doubly charged iodine ions appeared at the ionization energy $E_{el} > 30$ eV (the second ionization energy of iodine atom is 19.13 eV[14]). At temperatures higher than 650°C, the intensity of the iodine dimers substantially increases due to the gas-phase dimerization of iodine atoms:

$$2I(g) \Leftrightarrow I_2(g) \quad (3)$$

We also observed $[AgI]^+$ ions with total intensities (sum of the isotopes) of ca. 4% of monatomic iodine ions at 650°C and 15% at 750°C:

$$2AgI(s) \Leftrightarrow Ag(s) + I(g) + AgI(g) \quad (4)$$

It should be noted here that we did not observe $[Ag_nI_m]^+$ ions with $m, n > 1$ although the mass range and sensitivity of our experimental set-up would allow us to detect such ions. Metal halides in the form of M_nX_m, where M is metal and X is halogen, are typical as are intense vapour species under sublimation of pure metal halides like cesium iodide, for instance.[11,12] As a rule,[15] upon electron ionization of such species, one halogen is split off, with the formation of $[M_nX_{m-1}]^+$ ions. At the end of this pathway $[Ag]^+$ ions should also appear. However, these ions were not observed in our experiments despite the fact that the detection limit is 5×10^{-3} at. % for silver.[10] Sublimation of silver atoms from metallic silver, traces of which can be observed in the effusion cell after the tests, could not considered as an essential process since, according to literature,[16] the saturated vapour pressure over pure Ag does not exceed 10^{-4} Pa at 720°C.

The second component of the solid electrolyte, $AgPO_3$, also decomposed on the surface, but at a higher temperature than silver iodide. As a result, a variety of phosphorus oxide ions were detected. At the beginning of the heating, the sublimation of these species probably occurred in the form of the monoxide:

$$AgPO_3(s) \Leftrightarrow Ag(s) + PO(g) + O_2(g) \quad (5)$$

Then, above 650°C, the presence of ions from complex oxides such as $[P_4O_{10}]^+$, $[PO_2]^+$ and $[P_4O_9]^+$ became noticeable. It is general experience[6] that the equilibrium vapour over phosphorus-containing surfaces mainly consists of P_4O_{10} molecules. If this is the case, all above-mentioned ions might be formed upon electron ionization of P_4O_{10} molecules. In Table 2 and in Fig. 1 one can see that the apparent sublimation enthalpies of $[P_4O_{10}]^+$, $[PO_2]^+$ and $[P_4O_9]^+$ ions have approximately the same value, thus favouring our hypothesis on the generic origin of these ions.

Phosphorus dimer and tetramer ions appeared in the spectra at the temperature above 650°C, but with low intensity. Finally, it is probable that complex associative ions such as $[IPO_2]^+$, $[IP_2]^+$ and $[I_3P]^+$ were formed under molecular-viscous conditions (quasi-hydrodynamic flow), existing in the cell orifice under increased temperature and pressure, by means of association (conglomeration) of iodine- and phosphorus-containing molecules.

CONCLUSIONS

During the evaporation of the solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ we found that the dominant species in the electron ionization mass spectra below 600°C were iodine monomer ions with the apparent sublimation enthalpy $\Delta_s H = 155$ kJ mol^{-1}. At higher temperatures, the relative content of phosphorus oxide ions, mainly $[PO]^+$ and $[P_4O_{10}]^+$, with $\Delta_s H \sim 300$ kJ mol^{-1} increased. At even higher temperatures, silver iodide ions ($\Delta_s H \sim 125$ kJ mol^{-1}), iodine dimers ($\Delta_s H > 400$ kJ mol^{-1}) along with phosphorus dimers, tetramers ions and complex associative clusters $[IPO_2]^+$, $[IP_2]^+$ and $[I_3P]^+$ appeared. The solid electrolyte $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ turns out to be a stable and low-volatility substance at temperatures as high as 450°C. Then, in the temperature range from 500 to 650°C, the vapour phase over $(AgI)_{0.5}$-$(AgPO_3)_{0.5}$ is mainly composed of I, PO, P_4O_{10} and AgI molecules, which under electron ionization give birth to different iodine- and phosphorus-containing ion species. It is highly probable that the complex associative ions composed of iodine, phosphorus and phosphorus dioxide are formed in the molecular-viscous flow.

DOI: 10.1002/rcm

REFERENCES

1. Agrawal RC, Gupta RK. *J. Mat. Sci.* 1999; **34**: 1131.
2. Guo HX, Yang B, Chen L, Xia YD, Yin KB, Liu ZG, Yin J. *Appl. Phys. Lett.* 2007; **91**: 243513.
3. Escher C, Thomann S, Andreoli C, Fink H-W, Toquant J, Pohl DW. *Appl. Phys. Lett.* 2006; **89**: 053513.
4. Malugani JP, Wasniewski A, Doreau M, Robert G. *Mat. Res. Bull.* 1978; **13**: 427.
5. Roling B, Ingram MD, Lange M, Funke K. *Phys. Rev. B* 1997; **56**: 13619.
6. Sidorov LN, Korobov MV, Zhuravljova LV. *Mass Spectrometric Thermodynamic Investigations*. MSU: Moscow, 1985 (in Russian).
7. Hilpert K. *Fresenius J. Anal. Chem.* 2001; **370**: 471.
8. Drowart J, Chatillion C, Hastie J, Bonnell D. *Pure Appl. Chem.* 2005; **77**: 683.
9. Tolstogouzov A, Bardi U, Nishikawa O, Taniguchi M. *Surf. Interface Anal.* 2008; in press. DOI: 10.1002/sia.2906.
10. Bardi U, Niccolai F, Tosti M, Tolstogouzov A. *Int. J. Mass Spectrom.* 2008; **273**: 138. DOI: 10.1016/j.ijms.2008.03.013.
11. Butman MF, Kudin LS, Smirnov AA, Munir ZA. *Int. J. Mass Spectrom.* 2000; **202**: 121.
12. Viswanathan R, Hilpert K. *Ber. Bunsenges. Phys. Chem.* 1984; **88**: 125.
13. Demikhov KE, Pyzhov II. *Khimicheskoe Neftyanoe Mashinostroenie* 1977; No. 1: **26**(in Russian).
14. Available: http://physics.nist.gov/PhysRefData/Handbook/Tables/iodinetable1.htm (2008).
15. Bernauer O, Weil KG. *Ber. Bunsenges. Phys. Chem.* 1974; **78**: 161.
16. Wolf BH. *Handbook of Ion Sources*. CRC Press: Boca Raton, 1995.

DOI: 10.1002/rcm